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USE OF ALUMOZANE OLIGOMERS AS BINDERS IN THE PRODUCTION OF ALUMINONITRIDE CERAMICS

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It is demonstrated that almozane oligomers can be used as binders and plastifiers in the production of aluminum nitride articles by semidry molding. This allows for a simplification of the molding mixture technology and increases the mechanical strength of the articles.

In the context of the rapid progress in designing semiconductor equipment consuming large quantities of power, aluminum nitride is a promising material for producing highly heat-conducting ceramic substrates (instead of toxic beryllium oxide).

To obtain a material with good thermal and electrophysical properties, one should not only use a single-phase AlN powder, but also strive to increase the purity of the accompanying materials used in the production of ceramics, in particular, the technological binder. The existing technology is based on using synthetic caoutchouc as a plastifier in the form of a rubber adhesive. However, it creates certain technological difficulties related to preserving a constant concentration of the adhesive dissolved in benzene due to evaporation of the solvent and to protracted drying of suspension, preparation, and storage of the molding powder.

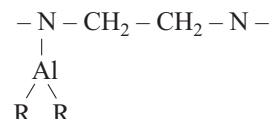
The molding power in storage becomes lumpy, its organic binder dries and forms rubber films and, consequently, the mixture becomes stratified. Molding of this powder without preliminary moistening and repeated granulation can result in a nonuniform distribution of caoutchouc in the volume of molded articles and in the emergence of defects (sealed porosity and air holes) in fired articles. The presence of cavities in a sintered material leads to the emergence of chips and microcracks in grinding, i.e., the purity of the product surface is disturbed. It is expedient to find a substitute for the binder that would meet the following requirements: nontoxicity, inertness to aluminum nitride, simplicity in introduction, sufficient strength of molded articles, and homogeneity of its structure.

Considering the above, almozane, oligomers whose properties and production methods were considered earlier [1], were selected. An additional advantage of these oligo-

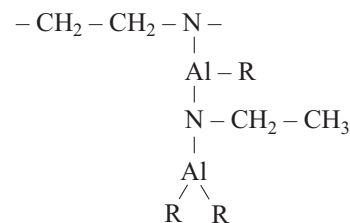
mers is the presence of $(-Al-N-)_n$ chains, which suggests that their decomposition can produce AlN in the process of firing.

The initial reactants for producing an almozane binder were a nitrogen-containing oligomer with the general formula $H_2N(CH_2CH_2NH)_nH$ ($n = 1-8$) and an organoaluminum monomer with the general formula AlR_3 ($R = C_2H_5$).

As a consequence of the reaction between the specified compounds, an almozane oligomer is formed:



In the course of its thermal treatment, an alkane (RH) is formed as a result of the condensation reaction, and bonds arise between individual oligomer chains, i.e., the oligomer chains are cross-linked:



Almozane oligomers are used in the form of solutions. The solvents in the present study were ethyl alcohol, acetyl acetate, and tetrahydrofuran.

To determine the possibility of using the almozane oligomer as a binder, its capacity for binding AlN powder and producing a sufficiently strong and homogeneous intermediate product in molding was investigated. For this purpose 1.5% (converted to dry matter) oligomer in the form of a 5% solution in one of the solvents was introduced into AlN

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TABLE 1

Binder and solvent	Density of nonfired material, g/cm ³	Strength of nonfired material, MPa
Caoutchouc in benzene	1.85 – 1.95	5 – 11
Alumozane oligomer:		
in ethyl alcohol	1.85 – 2.00	13 – 18
in ethyl acetate	2.00 – 2.05	10 – 20
in tetrahydrofuran	1.90 – 1.95	4 – 7

powder milled to a specific surface area of 1.0 – 1.2 m²/g and containing an activating additive of yttrium oxide in the amount of 1 – 2%. For reference purposes a solution of synthetic caoutchouc in benzene was used.

The choice of the most suitable solvent, which would preserve the main properties of alumozane oligomer, was based on the following parameters: duration of drying of the suspension; complete passing of a dried mixture through a sieve; density, strength, and air moisture resistance of molded articles.

The most technologically suitable was a binder based on the alumozane oligomer dissolved in ethyl alcohol. Using this solvent, the duration of drying of a molding mixture suitable for granulation is relatively short (1 – 2 h), whereas the drying duration for a suspension based on caoutchouc in benzene is 5 – 10 h (drying at room temperature in a drying cabinet). The dried mixture easily passed via a No. 008 sieve and the molding powder was homogeneous and fine-grained. The duration of drying of the suspension using ethyl acetate as a solvent lasted 3 – 5 h. The granulation of this molding mixture was not difficult either, and the molding power was fine-grained and homogeneous. When tetrahydrofuran was used as a solvent for the binder, the molding mixture resembled cement and strong solid heterogeneous granules ranging from 1 to 4 mm were formed. Only 50% of this power passed through a No. 008 sieve.

All obtained molding mixtures were compactible, and the density of nonfired materials was rather high [around 2.0 g/cm³ (Table 1)], and after the load was removed, no subsequent elastic expansion was registered. However, the powders containing ethyl acetate have to be especially thoroughly dried. Otherwise, when an external load is applied, the excessive solvent can be redistributed from the volume to the surface of the article.

Molded articles without visible defects were tested for tensile strength. The effect of the type of the binder on the density and mechanical tensile strength of molded aluminonitride ceramics is shown in Table 1.

The obtained data indicate that samples with alumozane oligomers on the whole are sufficiently strong for transportation and even stronger than samples molded with a plastifier in the form of caoutchouc dissolved in benzene. The structure of the samples was more homogeneous than the structure of the samples containing caoutchouc dissolved in benzene.

The resistance of the samples to the effect of air moisture was studied to determine the possibility of their long-time storage.

In storing the samples in air (after they were dried in a drying cabinet to a constant weight at 50°C for 2 h), the weight increment in the first day was 0.70% when using alumozane oligomer dissolved in ethyl alcohol and 0.04% when using caoutchouc dissolved in benzene. Later on, the weight increment continued but with a perceptible slowing and in total amounted to 0.9 and 0.4%, respectively, after exposure in air for 30 days.

The nearly an order of magnitude difference between the weight increment of the samples stored in air indicates that hydrolysis of AlN is more intense when alumozane oligomers are used as binders. Consequently, long-time storage of such intermediate products is possible only in an exsiccator.

The firing of samples was performed in a mixture of nitrogen and hydrogen at 1750 and 1850°C for 8 h. A comparison of the data obtained after firing samples with 1 and 2% yttrium oxide activating additive shows that sintering of samples with the alumozane oligomer on the whole is less intense than that of samples with the traditional binder. A ceramic material with a density close to the theoretical value could be obtained only by using a 2% additive of Y₂O₃ and a firing temperature of 1850°C. The sintered articles had a bending strength of 120 – 250 MPa and a thermal conductivity of 80 – 120 W/(m · K).

Thus, alumozane oligomers can be used with different solvents as binders in the production of molding powders and intermediate products of aluminonitride ceramics.

The replacement of the earlier used plastifier with the alumozane oligomer makes it possible to simplify the technology of producing the molding mixture and to increase the mechanical strength of the samples and the homogeneity of the structure of finished articles.

REFERENCES

1. N. N. Korneev, *Chemistry and Technology of Organoaluminum Compounds* [in Russian], Khimiya, Moscow (1979).